JC05 Rec'd PCT/PTO 27 MAR 2002

FORM PTO-1390
(REV. 5-93)

U.S DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

12093/887

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

U S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/089530

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/02666	**27 September 2000 (27.09.2000)**	**30 September 1999 (30.09.1999)**

TITLE OF INVENTION
ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR NUCLEAR FUEL ASSEMBLY WITH SAME

APPLICANT(S) FOR DO/EO/US
Daniel CHARQUET, Jean-Paul MARDON and Jean SENEVAT

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U S.C. 371
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U S C 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U S.C. 371(c)(3))
   a ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
   b. ☐ have been transmitted by the International Bureau
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U S.C. 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3 28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment
14. ☒ A substitute specification and marked-up version.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information International Search Report and International Preliminary Examination Report

Express Mail Label EV003628452US

NY01 462105 v 1

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U.S. APPLICATION NO. (if known, see 37 C.F.R.1.5) 10/089530	INTERNATIONAL APPLICATION NO PCT/FR00/02666	ATTORNEY'S DOCKET NUMBER 12093/887

17. ☒ The following fees are submitted

	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EUROPEAN PATENT OFFICE or JPO ..... $890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... $710.00 No international preliminary examination fee paid to USPTO (37 CFR 1 482) but international search fee paid to USPTO (37 CFR 1 445(a)(2)) ..... $740.00 Neither international preliminary examination fee (37 CFR 1 482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... $1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1 492(e)).	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	7 - 20 =	0	X $18 00	$ 0	
Independent Claims	5 - 3 =	2	X $84.00	$ 168	
Multiple dependent claim(s) (if applicable)			+ $280.00	$ 0	

TOTAL OF ABOVE CALCULATIONS =	$ 1058	
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).	$ 0	
SUBTOTAL =	$ 1058	
Processing fee of $130.00 for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1 492(f)). +	$ 0	
TOTAL NATIONAL FEE =	$ 1058	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40 00 per property +	$	
TOTAL FEES ENCLOSED =	$ 1058	
	Amount to be: refunded	$
	charged	$

a. ☐ A check in the amount of $__________ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 11-0600 in the amount of **$1058.00** to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0600. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

John M Vereb

SIGNATURE

SEND ALL CORRESPONDENCE TO:
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John M Vereb, Reg No 48,912

NAME

CUSTOMER NO. 26646

3/27/02

DATE

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[12093/887]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s)	:	Daniel CHARQUET et al.
Serial No.	:	To Be Assigned
Filed	:	Herewith
For	:	ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR NUCLEAR FUEL ASSEMBLY WITH SAME
Examiner	:	To Be Assigned
Art Unit	:	To Be Assigned

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT AND
37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT

S I R:

Kindly amend the above-captioned application before examination, as set forth below.

IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

IN THE CLAIMS:

On the first page of the claims, first line, please add
--WHAT IS CLAIMED IS:--.

Please cancel, without prejudice, claims 1 to 7 in the underlying PCT application.

Please add the following new claims:

EV003628452US

-- 8. (New) A zirconium-based alloy comprising:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron, from 0.8% to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and less than 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content lower than 3.

9. (New) The zirconium-based alloy according to claim 8, wherein the niobium is from 0.8% to 1.1% by weight, the iron from 0.3% to 0.35% by weight, the tin from 0.15% to 0.20% by weight, the at least one of chromium and vanadium from 0.01 to 0.1% by weight, the oxygen from 1000 to 1600 ppm, the sulphur from 5 to 35 ppm and the carbon less than 100 ppm.

10. (New) The zirconium-based alloy according to claim 8, where the oxygen is from 1000 to 1600 ppm.

11. (New) A cladding tube comprising:

an tubular arrangement of a zirconium-based alloy comprising:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron, from 0.8% to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and less than 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content lower than 3 in a recrystallized state.

12. (New) A flat product comprising:

a flat arrangement of a zirconium-based alloy comprising:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron, from 0.8% to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less

than 100 ppm carbon, from 5 to 35 ppm sulphur and less than 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content lower than 3 a recrystallized state.

13. (New) A method of manufacturing nuclear components comprising:

configuring components of a pressurized water reactor from an alloy comprising:

zirconium; and

in addition to unavoidable impurities, by weight, from 0.02 to 1% iron, from 0.8% to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and less than 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content lower than 3, wherein pressurized water initially contains less than 5 ppm of lithium.

14. (New) A method of making tubes that are configured to constitute at least one of all and the external portion of at least one of a nuclear fuel rod cladding and a guide tube for a nuclear fuel assembly comprising:

producing a bar from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% iron, from 0.8% to 2.3% niobium, less than 2000 ppm tin, less than 2000 ppm oxygen, less than 100 ppm carbon, from 5 to 35 ppm sulphur and less than 0.25% in total of at least one of chromium and vanadium, a ratio of a niobium content less 0.5% to an iron content and at least one of not supplemented and supplemented by at least one of a chromium and a vanadium content lower than 3;

water-quenching the bar after heating at from 1000°C to 1200°C;

extruding a blank after heating at from 600°C to 800°C;

cold-rolling in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and

carrying out a final thermal treatment at from 560°C to 620°C, all of the thermal treatments being carried out in at least one of an inert atmosphere and

under vacuum.--.

REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1 to 7 in the underlying PCT Application No. PCT/FR00/02666 and all claims in the International Preliminary Examination Report. This Preliminary Amendment adds new claims 8 to 14. The new claims, inter alia, conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(iii) and 1.125(b)(2), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/FR00/02666 includes an International Search Report, dated March 20, 2001, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

The underlying PCT Application No. PCT/FR00/02666 includes an International Preliminary Examination Report, dated July 13, 2001 and is included herewith.

It is respectfully submitted that the subject matter of the present application is new, non-obvious and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,

KENYON & KENYON

Dated: 3/27/02

By: John M. Vereb

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10/089530
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[12093/887]

ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR NUCLEAR FUEL ASSEMBLY WITH SAME

FIELD OF THE INVENTION

The present invention relates to zirconium-based alloys that are to constitute nuclear fuel assembly components usable in light-water nuclear reactors, such as nuclear fuel rod claddings or assembly guide tubes, or even flat products, such as grid plates.

The invention [has a particularly important]**may be used**, although not [exclusive]**exclusively**,[application] in the field of the manufacture of cladding tubes for fuel rods intended for [pressurised-water]**pressurized-water** reactors in which the risks of corrosion are particularly high as a result of a high lithium content and possibly as a result of risk of boiling, and also in the field of strip materials used for structural components of the fuel assemblies of such reactors. The invention also proposes a method for making such components.

BACKGROUND INFORMATION

Patent application PCT FR99/00737 proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.03 to 0.25% in total of iron, on the one hand, and of at least one of the elements of the group constituted by chromium and vanadium, on the other hand, having from 0.8 to 1.3% of niobium, less than 2000 ppm of tin, from 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 50 ppm of silicon, the ratio of the iron content, on the one hand, to the chromium or vanadium content, on the other hand, being from 0.5 to 30.

The invention is based on observations made by the inventors in the course of a systematic study of the intermetallic phases and the crystallographic forms of those phases which appear when the relative contents of iron and niobium are varied while the contents of tin, sulphur and oxygen are described in the application mentioned above. It is also based on the observation, made experimentally, that the nature and the crystallographic form of the intermetallic phases containing zirconium, iron and niobium have a major influence on corrosion resistance in various environments.

In particular, it has been found that the presence of compounds having a crystalline structure with a face-centered cubic lattice, obtained owing to a proportion of iron relative to niobium sufficient to result in the presence of $(Zr\ Nb)_4\ Fe_2$, at the expense of the compound $Zr\ (Nb,\ Fe)_2$ having a hexagonal lattice, and of the phase ßNb, which predominate at the high Nb/Fe ratios, substantially improves corrosion in a medium having a high lithium content, such as that which exists at the beginning of an operating cycle of some [pressurised-water]**pressurized-water** reactors. On the other hand, the presence of the phase having a face-centered cubic lattice in too large a quantity slightly impairs corrosion resistance in an aqueous medium.

SUMMARY

The present invention aims especially to provide an alloy which enables components to be obtained [whose]**wherein the** composition [can]**may** be adapted in an optimum manner to the conditions of use provided for and whose composition is not likely to hamper the manufacturing steps excessively.

To that end, the invention proposes, in particular, a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to

2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3.

The choice of the ratio R = (Nb-0.5%)/Fe+Cr+V results from the observation that the phase having a face-centered cubic lattice appears as soon as the relation between the content of Fe (and also of Cr and V if they are present) and the content of Nb is such that R is lower than a threshold which depends slightly on the contents of other elements and on the temperature but is at most 3.

The invention also proposes a method for making a tube according to which:

- a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3;
- the bar is water-quenched after heating at from 1000°C to 1200°C;
- a blank is extruded after heating at a temperature of from 600°C to 800°C;
- the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and
- a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

The final thermal treatment leaves the tube in the [recrystallised]**recrystallized** state, which promotes creep strength, without modifying the nature of the phases. The addition of chromium and/or vanadium, which is substituted for iron and niobium in the hexagonal phase, enables the proportion of the two phases, hexagonal and face-centered cubic, to be controlled.

The alloy may also be used to produce flat elements. Those elements are also used in the [recrystallised]**recrystallized** state and [can]**may** be manufactured by the following sequence: a blank is produced from a zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3,

the blank is cold-rolled in at least three passes, with intermediate thermal treatments and a final thermal treatment,

one of those intermediate thermal treatments or a preliminary thermal treatment before the first cold-rolling pass being effected for a long period of at least 2 hours at a temperature lower than 600°C, and

any thermal treatment following the long treatment and, in particular, the final [recrystallisation]**recrystallization** treatment, being effected at a temperature lower than 620°C.

The invention also proposes the application of the above alloy to the production of components of nuclear reactors operating with [pressurised]**pressurized** water that initially contains less than 5 ppm of lithium. Although that content then decreases rapidly, owing to its consumption in order to adjust

the pH of the coolant, it may be important to avoid rapid initial corrosion.

The existence of the intermetallic compounds, which is due to the presence of iron in a sufficient quantity, including the existence of Zr (Nb, Fe)$_2$, reduces the amount of niobium precipitates in phase ß which do not promote corrosion in a lithium-containing medium, but also the niobium content of the solid solution and therefore gives satisfactory resistance to uniform corrosion at a temperature of approximately 400°C, which is representative of the temperature that prevails in reactors.

The presence of chromium and/or vanadium as a very partial replacement for iron in the intermetallic precipitates of the type Zr (Nb, Fe, Cr, V)$_2$ has no marked effect on corrosion at 400°C because chromium and/or vanadium is simply substituted for iron and/or niobium in the intermetallic compound as the chromium content increases. The improved corrosion resistance at 400°C is maintained especially if the sum Fe+Cr (optionally plus vanadium) is at least 0.03%.

To [summarise]**summarize**, an alloy of the above type having a use in the recrystallised state to increase its resistance to the bi-axial creep of tubes and the aptitude for the pressing of sheet metal has characteristics which are adjustable by regulating the iron/niobium ratio but which are still favourable to:

- a high corrosion resistance in an aqueous medium at high temperature, which medium optionally contains lithium, the resistance being all the higher in this last-mentioned case if a high iron content is adopted, which is permitted by a high Nb content and with an iron/niobium ratio exceeding 0.3,
- a high creep strength owing to the presence of tin which remains at a very low content and, owing to doping with

oxygen, at a content lower than 2000 ppm, which then has no harmful effect on corrosion resistance.

In current reactors, the ranges given below are particularly valuable as a zirconium-based alloy also containing, by weight, apart from unavoidable impurities:

- Nb : 0.8% to 1.1% by weight
- Fe : 0.3% to 0.35% by weight
- Sn : 0.15% to 0.20% by weight
- Cr and/or V : 0.01 to 0.1% by weight
- O_2 : 1000 to 1600 ppm
- S : 5 to 35 ppm
- C : less than 100 ppm

BRIEF DESCRIPTION OF THE DRAWINGS

The above characteristics and others will emerge more clearly on reading the following description of particular embodiments which are given by way of non-limiting example. The description refers to the drawings which accompany it and in which:

[-]Figure 1 is a ternary diagram showing the intermetallic compounds and microstructures which appear for various ranges of composition, in the case of a content of 0.2% of tin, at a temperature of from 560°C to [620°C;]**620oc.**

[-]

Figure 2 [shows]**illustrates** a fraction of the diagram on a large scale[;

]**.**

[-]Figure 3 [shows]**illustrates** results of corrosion tests in a lithium-containing medium on samples having variable iron and niobium contents.

DETAILED DESCRIPTION

[The] **Referring to the figures, the** carbon and oxygen contents [were] **of obtained samples are** substantially identical for all of the samples and were lower than the maximum values given above. The tin content was 0.2% and the sulphur content was 10 ppm.

The samples were manufactured by thermo-metallurgical operations at a temperature not exceeding 620°C, any treatment exceeding that value beyond the extrusion operation reducing corrosion resistance at high temperature.

The ternary diagram in Figure 1 shows, for Fe/Nb ratios lower than approximately 0.3, the existence of a region in which the αZr phase (with the exclusion of the βZr phase which is very detrimental from the point of view of corrosion resistance), the βNb phase precipitates and the intermetallic phase $Zr\ (Nb, Fe)_2$, which has a hexagonal structure, co-exist.

For a high Fe/Nb ratio, up to a niobium content of the order of 50%, which is higher by more than one order of magnitude than the contents used, the compound $(Zr, Nb)_4Fe_2$, which is face-centered cubic, also appears. The βNb phase disappears completely only at a Fe/Nb ratio of the order of 0.6.

As will be seen hereinafter, it appeared that a high niobium content is very [favourable] **favorable** to corrosion resistance in lithium-containing water.

The coexistence of the cubic and hexagonal phases is promoted by a Fe/Nb ratio higher than 0.3, while respecting the relation (Nb-0.5%)/Fe+Cr+V > 2.5.

A precise study of the ternary diagram for the low Fe and Nb contents shows that the Nb content in solid solution develops with the Fe content, with Nb remaining constant.

As soon as the Fe [ ]content exceeds 60-70 ppm for the alloy according to the present invention, the hexagonal Zr $(Nb,Fe)_2$ form appears which substitutes the βNb phase for a ratio by weight of Nb/Fe substantially equal to 2.3.

There then appears the [face-centred]**face-centered** cubic compound $(Zr, Nb)_4Fe_2$, corresponding to Nb/Fe substantially equal to 0.6.

This face-centered cubic phase $(Zr, Nb)_4Fe_2$ starts to appear for:

1% Nb	from 0.29 to 0.44% Fe
1.5% Nb	from 0.49 to 0.66% Fe
2% Nb	beyond 0.78% Fe

The diagram shows that, by simultaneously increasing the content of Nb and of Fe, a higher density of intermetallics is obtained, which promotes corrosion in a lithium-containing medium.

The influence of the Fe and Nb contents is shown more clearly in Figure 3 which gives the measurement of the weight of alloy samples after maintenance for 84 days in water containing 70 ppm of lithium at a temperature of 360°C; the measurement of the weight of a sample of Zircaloy 4 under the same conditions was 35.96 mg/dm^2.

The value of the simultaneous presence of a high content of niobium and iron and of the observance of the condition explained above will be immediately appreciated.

[12093/887]

ABSTRACT

The invention proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3.

ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR NUCLEAR FUEL ASSEMBLY WITH SAME

FIELD OF THE INVENTION

The present invention relates to zirconium-based alloys that are to constitute nuclear fuel assembly components usable in light-water nuclear reactors, such as nuclear fuel rod claddings or assembly guide tubes, or even flat products, such as grid plates.

The invention may be used, although not exclusively, in the field of the manufacture of cladding tubes for fuel rods intended for pressurized-water reactors in which the risks of corrosion are particularly high as a result of a high lithium content and possibly as a result of risk of boiling, and also in the field of strip materials used for structural components of the fuel assemblies of such reactors. The invention also proposes a method for making such components.

BACKGROUND INFORMATION

Patent application PCT FR99/00737 proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.03 to 0.25% in total of iron, on the one hand, and of at least one of the elements of the group constituted by chromium and vanadium, on the other hand, having from 0.8 to 1.3% of niobium, less than 2000 ppm of tin, from 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 50 ppm of silicon, the ratio of the iron content, on the one hand, to the chromium or vanadium content, on the other hand, being from 0.5 to 30.

The invention is based on observations made by the inventors in the course of a systematic study of the intermetallic phases and the crystallographic forms of those phases which appear when the relative contents of iron and niobium are varied while the contents of tin, sulphur and oxygen are described in the application mentioned above. It is also based on the observation, made experimentally, that the nature and the crystallographic form of the intermetallic phases containing zirconium, iron and niobium have a major influence on corrosion resistance in various environments.

In particular, it has been found that the presence of compounds having a crystalline structure with a face-centered cubic lattice, obtained owing to a proportion of iron relative to niobium sufficient to result in the presence of $(Zr\ Nb)_4\ Fe_2$, at the expense of the compound Zr $(Nb,\ Fe)_2$ having a hexagonal lattice, and of the phase ßNb, which predominate at the high Nb/Fe ratios, substantially improves corrosion in a medium having a high lithium content, such as that which exists at the beginning of an operating cycle of some pressurized-water reactors. On the other hand, the presence of the phase having a face-centered cubic lattice in too large a quantity slightly impairs corrosion resistance in an aqueous medium.

SUMMARY

The present invention aims especially to provide an alloy which enables components to be obtained wherein the composition may be adapted in an optimum manner to the conditions of use provided for and whose composition is not likely to hamper the manufacturing steps excessively.

To that end, the invention proposes, in particular, a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3.

The choice of the ratio R = (Nb-0.5%)/Fe+Cr+V results from the observation that the phase having a face-centered cubic lattice appears as soon as the relation between the content of Fe (and also of Cr and V if they are present) and the content of Nb is such that R is lower than a threshold which depends slightly on the contents of other elements and on the temperature but is at most 3.

The invention also proposes a method for making a tube according to which:

- a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3;
- the bar is water-quenched after heating at from 1000°C to 1200°C;
- a blank is extruded after heating at a temperature of from 600°C to 800°C;

- the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and

- a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

The final thermal treatment leaves the tube in the recrystallized state, which promotes creep strength, without modifying the nature of the phases. The addition of chromium and/or vanadium, which is substituted for iron and niobium in the hexagonal phase, enables the proportion of the two phases, hexagonal and face-centered cubic, to be controlled.

The alloy may also be used to produce flat elements. Those elements are also used in the recrystallized state and may be manufactured by the following sequence: a blank is produced from a zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3,

the blank is cold-rolled in at least three passes, with intermediate thermal treatments and a final thermal treatment,

one of those intermediate thermal treatments or a preliminary thermal treatment before the first cold-rolling

pass being effected for a long period of at least 2 hours at a temperature lower than 600°C, and

any thermal treatment following the long treatment and, in particular, the final recrystallization treatment, being effected at a temperature lower than 620°C.

The invention also proposes the application of the above alloy to the production of components of nuclear reactors operating with pressurized water that initially contains less than 5 ppm of lithium. Although that content then decreases rapidly, owing to its consumption in order to adjust the pH of the coolant, it may be important to avoid rapid initial corrosion.

The existence of the intermetallic compounds, which is due to the presence of iron in a sufficient quantity, including the existence of $Zr (Nb, Fe)_2$, reduces the amount of niobium precipitates in phase ß which do not promote corrosion in a lithium-containing medium, but also the niobium content of the solid solution and therefore gives satisfactory resistance to uniform corrosion at a temperature of approximately 400°C, which is representative of the temperature that prevails in reactors.

The presence of chromium and/or vanadium as a very partial replacement for iron in the intermetallic precipitates of the type $Zr (Nb, Fe, Cr, V)_2$ has no marked effect on corrosion at 400°C because chromium and/or vanadium is simply substituted for iron and/or niobium in the intermetallic compound as the chromium content increases. The improved corrosion resistance at 400°C is maintained especially if the sum Fe+Cr (optionally plus vanadium) is at least 0.03%.

To summarize, an alloy of the above type having a use in the recrystallised state to increase its resistance to the bi-axial creep of tubes and the aptitude for the pressing of sheet metal has characteristics which are adjustable by regulating the iron/niobium ratio but which are still favourable to:

- a high corrosion resistance in an aqueous medium at high temperature, which medium optionally contains lithium, the resistance being all the higher in this last-mentioned case if a high iron content is adopted, which is permitted by a high Nb content and with an iron/niobium ratio exceeding 0.3,
- a high creep strength owing to the presence of tin which remains at a very low content and, owing to doping with oxygen, at a content lower than 2000 ppm, which then has no harmful effect on corrosion resistance.

In current reactors, the ranges given below are particularly valuable as a zirconium-based alloy also containing, by weight, apart from unavoidable impurities:

- Nb : 0.8% to 1.1% by weight
- Fe : 0.3% to 0.35% by weight
- Sn : 0.15% to 0.20% by weight
- Cr and/or V : 0.01 to 0.1% by weight
- O_2 : 1000 to 1600 ppm
- S : 5 to 35 ppm
- C : less than 100 ppm

BRIEF DESCRIPTION OF THE DRAWINGS

The above characteristics and others will emerge more clearly on reading the following description of particular

embodiments which are given by way of non-limiting example. The description refers to the drawings which accompany it and in which:

Figure 1 is a ternary diagram showing the intermetallic compounds and microstructures which appear for various ranges of composition, in the case of a content of 0.2% of tin, at a temperature of from 560°C to 620oc.

Figure 2 illustrates a fraction of the diagram on a large scale.

Figure 3 illustrates results of corrosion tests in a lithium-containing medium on samples having variable iron and niobium contents.

DETAILED DESCRIPTION

Referring to the figures, the carbon and oxygen contents of obtained samples are substantially identical for all of the samples and were lower than the maximum values given above. The tin content was 0.2% and the sulphur content was 10 ppm.

The samples were manufactured by thermo-metallurgical operations at a temperature not exceeding 620°C, any treatment exceeding that value beyond the extrusion operation reducing corrosion resistance at high temperature.

The ternary diagram in Figure 1 shows, for Fe/Nb ratios lower than approximately 0.3, the existence of a region in which the αZr phase (with the exclusion of the βZr phase which is very detrimental from the point of view of corrosion resistance), the βNb phase precipitates and the

intermetallic phase Zr $(Nb, Fe)_2$, which has a hexagonal structure, co-exist.

For a high Fe/Nb ratio, up to a niobium content of the order of 50%, which is higher by more than one order of magnitude than the contents used, the compound $(Zr, Nb)_4Fe_2$, which is face-centered cubic, also appears. The βNb phase disappears completely only at a Fe/Nb ratio of the order of 0.6.

As will be seen hereinafter, it appeared that a high niobium content is very favorable to corrosion resistance in lithium-containing water.

The coexistence of the cubic and hexagonal phases is promoted by a Fe/Nb ratio higher than 0.3, while respecting the relation (Nb-0.5%)/Fe+Cr+V > 2.5.

A precise study of the ternary diagram for the low Fe and Nb contents shows that the Nb content in solid solution develops with the Fe content, with Nb remaining constant.

As soon as the Fe content exceeds 60-70 ppm for the alloy according to the present invention, the hexagonal Zr $(Nb,Fe)_2$ form appears which substitutes the βNb phase for a ratio by weight of Nb/Fe substantially equal to 2.3.

There then appears the face-centered cubic compound $(Zr, Nb)_4Fe_2$, corresponding to Nb/Fe substantially equal to 0.6.

This face-centered cubic phase $(Zr, Nb)_4Fe_2$ starts to appear for:

1% Nb   from 0.29 to 0.44% Fe

1.5% Nb	from 0.49 to 0.66% Fe
2% Nb	beyond 0.78% Fe

The diagram shows that, by simultaneously increasing the content of Nb and of Fe, a higher density of intermetallics is obtained, which promotes corrosion in a lithium-containing medium.

The influence of the Fe and Nb contents is shown more clearly in Figure 3 which gives the measurement of the weight of alloy samples after maintenance for 84 days in water containing 70 ppm of lithium at a temperature of 360°C; the measurement of the weight of a sample of Zircaloy 4 under the same conditions was 35.96 mg/dm^2.

The value of the simultaneous presence of a high content of niobium and iron and of the observance of the condition explained above will be immediately appreciated.

ABSTRACT

The invention proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3.

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ZIRCONIUM-BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR NUCLEAR FUEL ASSEMBLY WITH SAME

The present invention relates to zirconium-based alloys that are to constitute nuclear fuel assembly components usable in light-water nuclear reactors, such as nuclear fuel rod claddings or assembly guide tubes, or even flat products, such as grid plates.

The invention has a particularly important, although not exclusive, application in the field of the manufacture of cladding tubes for fuel rods intended for pressurised-water reactors in which the risks of corrosion are particularly high as a result of a high lithium content and possibly as a result of risk of boiling, and also in the field of strip materials used for structural components of the fuel assemblies of such reactors. The invention also proposes a method for making such components.

Patent application PCT FR99/00737 proposes a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.03 to 0.25% in total of iron, on the one hand, and of at least one of the elements of the group constituted by chromium and vanadium, on the other hand, having from 0.8 to 1.3% of niobium, less than 2000 ppm of tin, from 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 50 ppm of silicon, the ratio of the iron content, on the one hand, to the chromium or vanadium content, on the other hand, being from 0.5 to 30.

The invention is based on observations made by the inventors in the course of a systematic study of the intermetallic phases and the crystallographic forms of those phases which

appear when the relative contents of iron and niobium are varied while the contents of tin, sulphur and oxygen are described in the application mentioned above. It is also based on the observation, made experimentally, that the nature and the crystallographic form of the intermetallic phases containing zirconium, iron and niobium have a major influence on corrosion resistance in various environments.

In particular, it has been found that the presence of compounds having a crystalline structure with a face-centered cubic lattice, obtained owing to a proportion of iron relative to niobium sufficient to result in the presence of $(Zr\ Nb)_4\ Fe_2$, at the expense of the compound $Zr\ (Nb,\ Fe)_2$ having a hexagonal lattice, and of the phase ßNb, which predominate at the high Nb/Fe ratios, substantially improves corrosion in a medium having a high lithium content, such as that which exists at the beginning of an operating cycle of some pressurised-water reactors. On the other hand, the presence of the phase having a face-centered cubic lattice in too large a quantity slightly impairs corrosion resistance in an aqueous medium.

The present invention aims especially to provide an alloy which enables components to be obtained whose composition can be adapted in an optimum manner to the conditions of use provided for and whose composition is not likely to hamper the manufacturing steps excessively.

To that end, the invention proposes, in particular, a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium

and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3.

The choice of the ratio R = (Nb-0.5%)/Fe+Cr+V results from the observation that the phase having a face-centered cubic lattice appears as soon as the relation between the content of Fe (and also of Cr and V if they are present) and the content of Nb is such that R is lower than a threshold which depends slightly on the contents of other elements and on the temperature but is at most 3.

The invention also proposes a method for making a tube according to which:

- a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3;
- the bar is water-quenched after heating at from 1000°C to 1200°C;
- a blank is extruded after heating at a temperature of from 600°C to 800°C;
- the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and
- a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

The final thermal treatment leaves the tube in the recrystallised state, which promotes creep strength, without modifying the nature of the phases. The addition of chromium and/or vanadium, which is substituted for iron and niobium in the hexagonal phase, enables the proportion of the two phases, hexagonal and face-centered cubic, to be controlled.

The alloy may also be used to produce flat elements. Those elements are also used in the recrystallised state and can be manufactured by the following sequence: a blank is produced from a zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio R of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3,

the blank is cold-rolled in at least three passes, with intermediate thermal treatments and a final thermal treatment,

one of those intermediate thermal treatments or a preliminary thermal treatment before the first cold-rolling pass being effected for a long period of at least 2 hours at a temperature lower than 600°C, and

any thermal treatment following the long treatment and, in particular, the final recrystallisation treatment, being effected at a temperature lower than 620°C.

The invention also proposes the application of the above alloy to the production of components of nuclear reactors operating with pressurised water that initially contains

less than 5 ppm of lithium. Although that content then decreases rapidly, owing to its consumption in order to adjust the pH of the coolant, it may be important to avoid rapid initial corrosion.

The existence of the intermetallic compounds, which is due to the presence of iron in a sufficient quantity, including the existence of $Zr\ (Nb,\ Fe)_2$, reduces the amount of niobium precipitates in phase ß which do not promote corrosion in a lithium-containing medium, but also the niobium content of the solid solution and therefore gives satisfactory resistance to uniform corrosion at a temperature of approximately 400°C, which is representative of the temperature that prevails in reactors.

The presence of chromium and/or vanadium as a very partial replacement for iron in the intermetallic precipitates of the type $Zr\ (Nb,\ Fe,\ Cr,\ V)_2$ has no marked effect on corrosion at 400°C because chromium and/or vanadium is simply substituted for iron and/or niobium in the intermetallic compound as the chromium content increases. The improved corrosion resistance at 400°C is maintained especially if the sum Fe+Cr (optionally plus vanadium) is at least 0.03%.

To summarise, an alloy of the above type having a use in the recrystallised state to increase its resistance to the bi-axial creep of tubes and the aptitude for the pressing of sheet metal has characteristics which are adjustable by regulating the iron/niobium ratio but which are still favourable to:

- a high corrosion resistance in an aqueous medium at high temperature, which medium optionally contains lithium, the resistance being all the higher in this last-mentioned case if a high iron content is adopted, which is permitted

by a high Nb content and with an iron/niobium ratio exceeding 0.3,

- a high creep strength owing to the presence of tin which remains at a very low content and, owing to doping with oxygen, at a content lower than 2000 ppm, which then has no harmful effect on corrosion resistance.

In current reactors, the ranges given below are particularly valuable as a zirconium-based alloy also containing, by weight, apart from unavoidable impurities:

- Nb : 0.8% to 1.1% by weight
- Fe : 0.3% to 0.35% by weight
- Sn : 0.15% to 0.20% by weight
- Cr and/or V : 0.01 to 0.1% by weight
- O_2 : 1000 to 1600 ppm
- S : 5 to 35 ppm
- C : less than 100 ppm

The above characteristics and others will emerge more clearly on reading the following description of particular embodiments which are given by way of non-limiting example. The description refers to the drawings which accompany it and in which:

- Figure 1 is a ternary diagram showing the intermetallic compounds and microstructures which appear for various ranges of composition, in the case of a content of 0.2% of tin, at a temperature of from 560°C to 620°C;
- Figure 2 shows a fraction of the diagram on a large scale;
- Figure 3 shows results of corrosion tests in a lithium-containing medium on samples having variable iron and niobium contents.

The carbon and oxygen contents were substantially identical for all of the samples and were lower than the maximum values given above. The tin content was 0.2% and the sulphur content was 10 ppm.

The samples were manufactured by thermo-metallurgical operations at a temperature not exceeding 620°C, any treatment exceeding that value beyond the extrusion operation reducing corrosion resistance at high temperature.

The ternary diagram in Figure 1 shows, for Fe/Nb ratios lower than approximately 0.3, the existence of a region in which the αZr phase (with the exclusion of the βZr phase which is very detrimental from the point of view of corrosion resistance), the βNb phase precipitates and the intermetallic phase Zr $(Nb, Fe)_2$, which has a hexagonal structure, co-exist.

For a high Fe/Nb ratio, up to a niobium content of the order of 50%, which is higher by more than one order of magnitude than the contents used, the compound $(Zr, Nb)_4Fe_2$, which is face-centered cubic, also appears. The βNb phase disappears completely only at a Fe/Nb ratio of the order of 0.6.

As will be seen hereinafter, it appeared that a high niobium content is very favourable to corrosion resistance in lithium-containing water.

The coexistence of the cubic and hexagonal phases is promoted by a Fe/Nb ratio higher than 0.3, while respecting the relation $(Nb-0.5\%)/Fe+Cr+V > 2.5$.

A precise study of the ternary diagram for the low Fe and Nb contents shows that the Nb content in solid solution develops with the Fe content, with Nb remaining constant.

As soon as the Fe content exceeds 60-70 ppm for the alloy according to the present invention, the hexagonal Zr $(Nb,Fe)_2$ form appears which substitutes the βNb phase for a ratio by weight of Nb/Fe substantially equal to 2.3.

There then appears the face-centred cubic compound $(Zr, Nb)_4Fe_2$, corresponding to Nb/Fe substantially equal to 0.6.

This face-centered cubic phase $(Zr, Nb)_4Fe_2$ starts to appear for:

1% Nb	from 0.29 to 0.44% Fe
1.5% Nb	from 0.49 to 0.66% Fe
2% Nb	beyond 0.78% Fe

The diagram shows that, by simultaneously increasing the content of Nb and of Fe, a higher density of intermetallics is obtained, which promotes corrosion in a lithium-containing medium.

The influence of the Fe and Nb contents is shown more clearly in Figure 3 which gives the measurement of the weight of alloy samples after maintenance for 84 days in water containing 70 ppm of lithium at a temperature of 360°C; the measurement of the weight of a sample of Zircaloy 4 under the same conditions was 35.96 mg/dm^2.

The value of the simultaneous presence of a high content of niobium and iron and of the observance of the condition explained above will be immediately appreciated.

Claims

1. Zirconium-based alloy also containing, by weight, in addition to unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3.

2. Alloy according to claim 1, also containing from 0.8% to 1.1% by weight of niobium, from 0.3% to 0.35% by weight of iron, from 0.15% to 0.20% by weight of tin, from 0.01 to 0.1% by weight of chromium and/or vanadium, from 1000 to 1600 ppm of oxygen, from 5 to 35 ppm of sulphur and less than 100 ppm of carbon.

3. Alloy according to claim 1, containing 1000 - 1600 ppm of oxygen.

4. Cladding tube made from an alloy according to claim 1, 2 or 3, in the recrystallised state.

5. Flat product made from an alloy according to claim 1, 2 or 3, in the recrystallised state.

6. Application of the alloy according to any one of claims 1, 2 and 3, to the production of components of nuclear reactors operating with pressurised water that initially contains less than 5 ppm of lithium.

7. Method for making tubes that are to constitute all or the external portion of a nuclear fuel rod cladding or a

guide tube for a nuclear fuel assembly, characterised in that:

a bar is produced from a zirconium-based alloy also containing, by weight, apart from unavoidable impurities, from 0.02 to 1% of iron, from 0.8% to 2.3% of niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than 0.25% in total of chromium and/or vanadium, the ratio of the niobium content less 0.5% to the iron content, optionally supplemented by the chromium and/or vanadium content, being lower than 3;

the bar is water-quenched after heating at from 1000°C to 1200°C;

a blank is extruded after heating at from 600°C to 800°C;

the blank is cold-rolled in at least two passes to obtain a tube, with intermediate thermal treatments at from 560°C to 620°C; and

a final thermal treatment is carried out at from 560°C to 620°C, all of the thermal treatments being carried out in an inert atmosphere or under vacuum.

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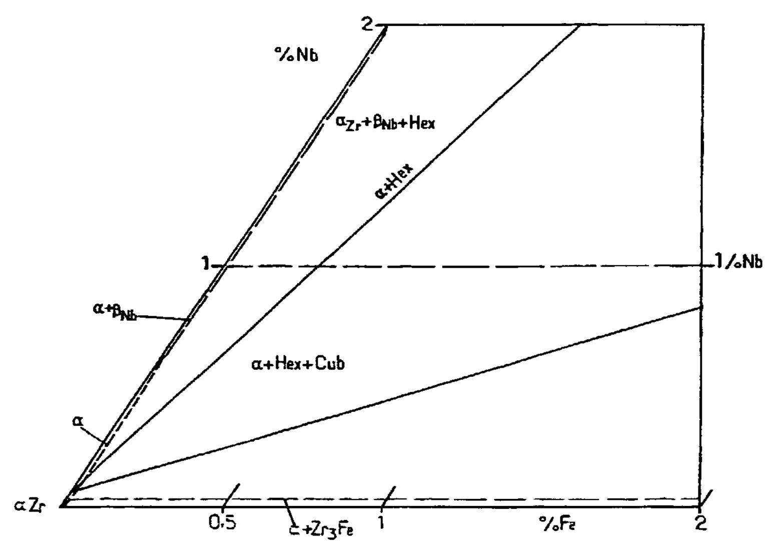
[Suite sur la page suivante]

(54) Title: ZIRCONIUM BASED ALLOY AND METHOD FOR MAKING A COMPONENT FOR NUCLEAR FUEL ASSEMBLY WITH SAME

(54) Titre: ALLIAGE A BASE DE ZIRCONIUM ET PROCEDE DE FABRICATION DE COMPOSANT POUR ASSEMBLAGE DE COMBUSTIBLE NUCLEAIRE EN UN TEL ALLIAGE



(57) Abstract: The invention concerns a zirconium alloy, containing, besides unavoidable impurities, 0.02 to 1 % iron, 0.8 to 2.3 % niobium, less than 2000 ppm of tin, less than 2000 ppm of oxygen, less than 100 ppm of carbon, from 5 to 35 ppm of sulphur and less than a total of 0.25 % of chromium and/or vanadium. The ratio of niobium content over iron content, optionally completed with chromium and/or vanadium content, is less than 3. The invention is applicable to nuclear reactor components.

[Suite sur la page suivante]

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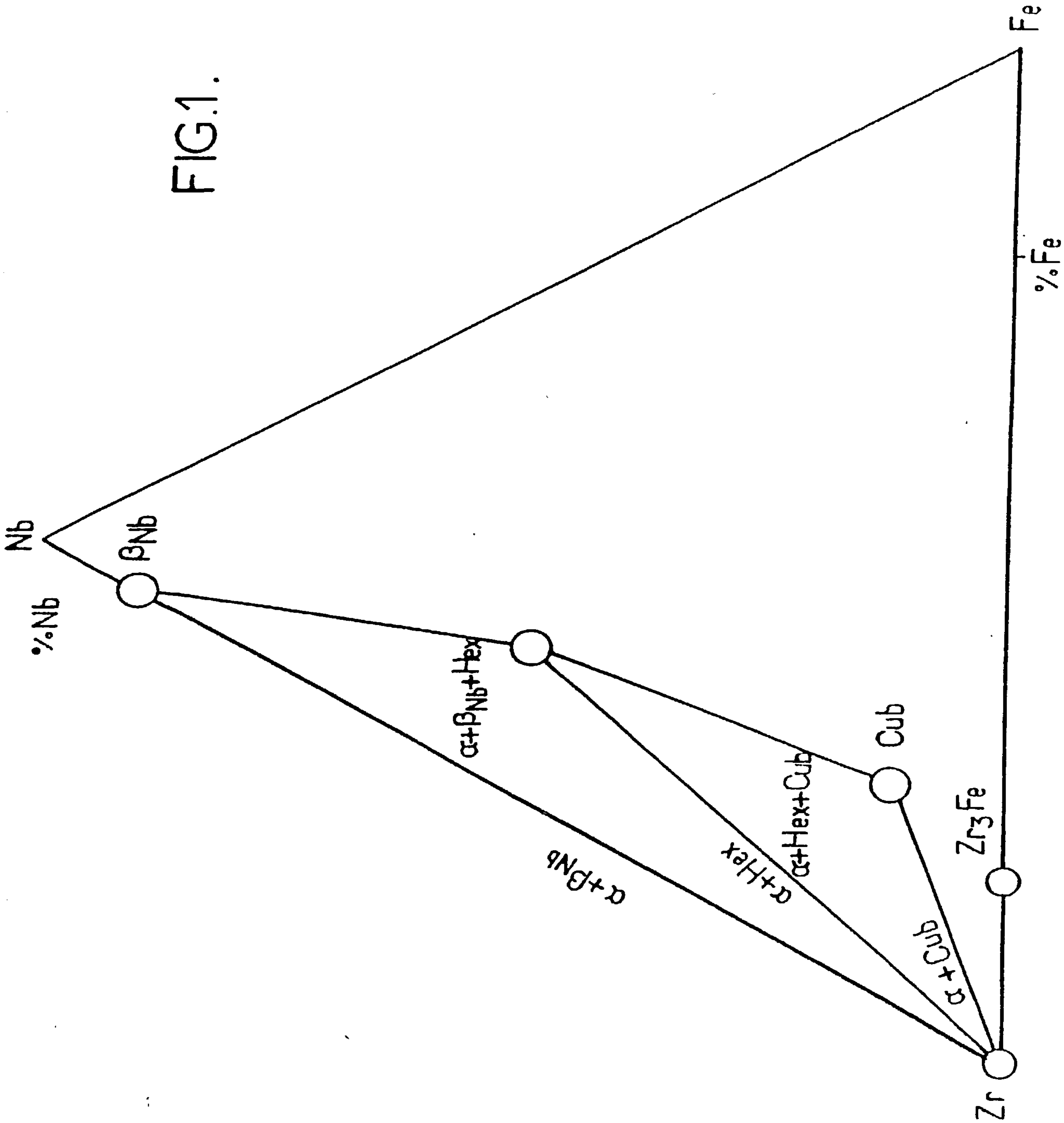
FIG.1.



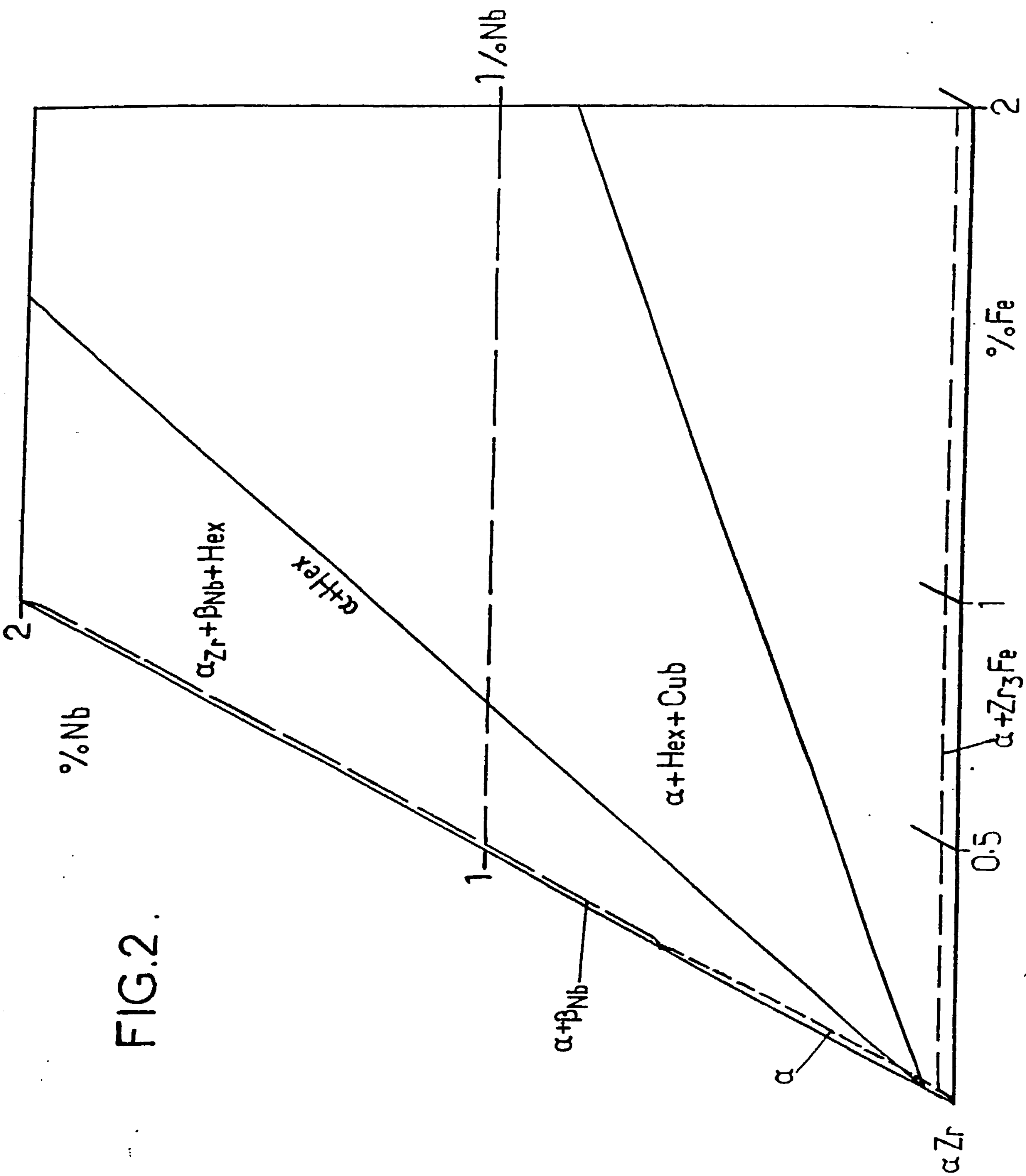


FIG.2.

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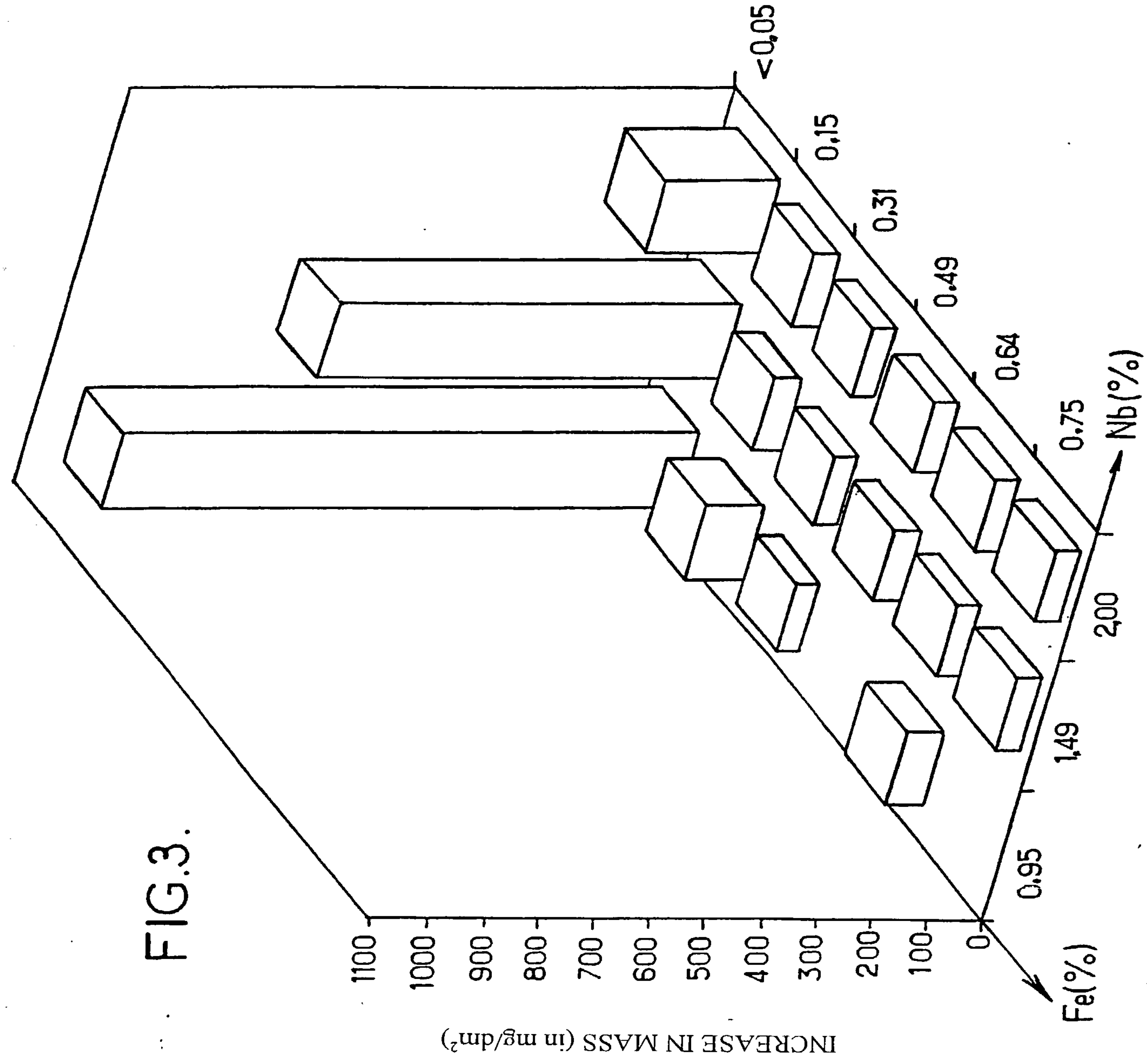

FIG.3.

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

DECLARATION AND POWER OF ATTORNEY

ATTORNEY'S DOCKET NO.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled Zirconium-based alloy and method for making a component for nuclear fuel assembly with same the specification of which

_____ is attached hereto.

X was filed on SEPTEMBER 27, 2000 as
United States Application Number or PCT International
Application Number PCT/FR00/02666
and was amended on ______________________
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

PRIOR FOREIGN APPLICATION(S)

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	DATE OF ISSUE (day, month, year)	PRIORITY CLAIMED UNDER 35 U S.C. § 119
FRANCE	99 12247	30/09/99		YES

PRIOR UNITED STATES APPLICATION(S)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

APPLICATION NUMBER	FILING DATE (day, month, year)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION NUMBER	FILING DATE (day, month, year)	STATUS (i e. Patented, Pending, Abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys:

3

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I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1-00

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Signature		Date	20/07/02

2-00

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Signature	Mardon J.P	Date	20/07/02

3-00

FULL NAME OF INVENTOR	FAMILY NAME SENEVAT	FIRST GIVEN NAME Jean	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY ANNECY FRX	STATE OR FOREIGN COUNTRY FRANCE	COUNTRY OF CITIZENSHIP FRENCH
POST OFFICE ADDRESS	POST OFFICE ADDRESS 39 rue Sommeiller	CITY ANNECY	STATE & ZIP CODE/COUNTRY 73400
Signature		Date 20/07/02	
FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
Signature		Date	

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